

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/GB05/000847

International filing date: 04 March 2005 (04.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: GB
Number: 0406037.2
Filing date: 18 March 2004 (18.03.2004)

Date of receipt at the International Bureau: 02 May 2005 (02.05.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



G805/86+



INVESTOR IN PEOPLE

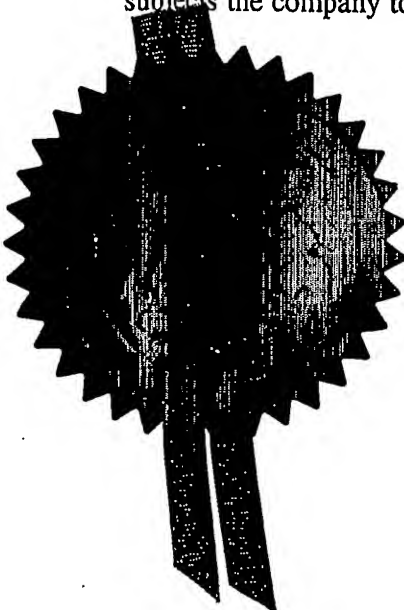
The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Dated 23 March 2005

Patents Form 1/77

Patents Act 1997
(Rule 16)The
Patent
Office

1/77

Request for grant of a patent

(see the notes on the back of this form. You can also get
an explanatory leaflet from the Patent office to help
you fill in this form)THE PATENT OFFICE
JR
18 MAR 2004
RECEIVED BY FAX

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1 Your reference

UOI 51130

2 Patent application number
(The Patent Office will fill in this part)

0406037.2

18 MAR 2004

3 Full name, address and postcode of the or of
each applicant (underline all surnames)Imperial Chemical Industries PLC
20 Manchester Square, London, W1U 3AN

Patents ADP Number (if you know it)

935 006

If the applicant is a corporate body, give the
country/state of its incorporation

United Kingdom

4 Title of the invention

Metal Oxide Dispersion

5 Name of Your Agent (if you have one)

HUMPHRIES, Martyn

"Address for service" in the United Kingdom
to which all correspondence should be sent
(including the postcode)Uniqema Intellectual Property Dept
Wilton Centre
Wilton
Redcar
England, TS10 4RF

Patents ADP Number (if you know it)

7896889002

6 If you are declaring priority from one or more
earlier patent applications, give the country
and the date of filing of the or each of theseCountry Priority Application number
(if you know it) Date of Filing
(day / month / year)7 If this application is divided or otherwise derived from an
earlier UK application, give the number and filing date of
the earlier applicationNumber of earlier application Date of Filing
(day / month / year)8 Is a statement of inventorship and of right to grant of a
patent required in support of this request?

Yes

Answer yes if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

See Note (d)

Patents Form 1/77

Patents Form 1/77

- 9 Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	-
Description	13
Claim(s)	4
Abstract	1
Drawings	-

- 10 If you are also filing any of the following state how many against each item

Priority documents	
Translations of priority documents	
Statement of Invention and right to grant of a patent (Patents Form 7/77)	
Request for Preliminary Examination and search (Patents Form 9/77)	
Request for Substantive Examination (Patents Form 10/77)	
Any other documents (Please specify)	

11

I/We request the grant of a patent on the basis of this application

Signature

Date 18.03.04

- 12 Name and daytime telephone number of person to contact in the United Kingdom

HUMPHRIES, Martyn
01642 435337

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 23 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been issued, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

UQI 51130

1

Metal Oxide Dispersion**Field of Invention**

- 5 The present invention relates to a dispersion of metal oxide particles, and in particular to the use thereof in a sunscreen product.

Background

- 10 Metal oxides such as titanium dioxide, zinc oxide and iron oxide have been employed as attenuators of ultraviolet light in sunscreens. Due to the increased awareness of the link between ultraviolet light and skin cancer, there has been an increasing requirement for ultraviolet light protection in everyday skincare and cosmetics products. There is a need for a metal oxide in a form which when incorporated into sunscreen products exhibits effective UV
- 15 absorption properties, be transparent in use, and have a pleasant skin feel. It is an extremely challenging problem to provide a product with all of these properties. There is a constant need in the market place to improve these properties, particularly transparency and skin feel.

Summary of the Invention

20

We have now surprisingly discovered an improved metal oxide dispersion, which overcomes or significantly reduces at least one of the aforementioned problems.

- 25 Accordingly, the present invention provides a dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of at least one polar material having an interfacial tension of less than 30 mNm^{-1} and at least one non-polar material having an interfacial tension of greater than 30 mNm^{-1} .

- 30 The present invention also provides a dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of (i) at least one polar material selected from the group consisting of, C12-15 alkyl benzoate, caprylic/capric triglyceride, cetearyl isononanoate, ethylhexyl isostearate, ethylhexyl palmitate, isononyl isononanoate, isopropyl isostearate, isopropyl myristate, isostearyl isostearate, isostearyl neopentanoate, octyldodecanol, pentaerythrityl
- 35 tetraisostearate, PPG-15 stearyl ether, triethylhexyl triglyceride, dicaprylyl carbonate, ethylhexyl stearate, helianthus annuus (sunflower) seed oil, isopropyl palmitate, and octyldodecyl neopentanoate, and (ii) at least one non-polar material selected from the group consisting of,

UQI 51130

2

C13-14 isoparaffin, isohexadecane, paraffinum liquidum (mineral oil), squalane, squalene, hydrogenated polyisobutene, and polydecene.

5 The present invention further provides a sunscreen product formed from a dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of at least one polar material having an interfacial tension of less than 30 mNm^{-1} and at least one non-polar material having an interfacial tension of greater than 30 mNm^{-1} .

10 The present invention further provides a sunscreen product comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, and (i) at least one polar material selected from the group consisting of are triethylhexyl triglyceride, C12-15 alkyl benzoate, caprylic/capric triglyceride, Isononyl Isononanoate, isostearyl neopentanoate, and octyldodecyl neopentanoate, and (ii) at least one non-polar material selected from the group
15 consisting of isohexadecane, hydrogenated polyisobutene, and squalane.

The invention yet further provides the use of a dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of at least one polar material having an interfacial tension
20 of less than 30 mNm^{-1} and at least one non-polar material having an interfacial tension of greater than 30 mNm^{-1} , to produce a sunscreen having improved skin feel.

The invention still further provides the use of a dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of at least one polar material having an interfacial tension
25 of less than 30 mNm^{-1} and at least one non-polar material having an interfacial tension of greater than 30 mNm^{-1} , in the manufacture of a transparent sunscreen having improved skin feel.

30 Preferably the metal oxide used in the present invention comprises an oxide of titanium, zinc or iron, and most preferably the metal oxide is titanium dioxide.

The preferred titanium dioxide particles comprise anatase and/or rutile crystal form. The titanium dioxide in the particles preferably comprises a major portion of rutile, more preferably
35 greater than 60% by weight, particularly greater than 70%, and especially greater than 80% by weight of rutile. The titanium dioxide in the particles preferably comprises in the range from 0.01 to 5%, more preferably 0.1 to 2%, and particularly 0.2 to 0.5% by weight of anatase. In addition, the titanium dioxide in the particles preferably comprises less than 40%, more preferably less than 30%, and particularly less than 25% by weight of amorphous titanium

UQI.51130

3

dioxide. The basic particles may be prepared by standard procedures, such as using the chloride process, or by the sulphate process, or by hydrolysis of an appropriate titanium compound such as titanium oxydichloride or an organic or inorganic titanate, or by oxidation of an oxidisable titanium compound, e.g. in the vapour state. The titanium dioxide particles are preferably prepared by the hydrolysis of a titanium compound, particularly of titanium oxydichloride.

The particles of metal oxide used in the present invention are preferably hydrophobic. The hydrophobicity of the metal oxide can be determined by pressing a disc of metal oxide powder, and measuring the contact angle of a drop of water placed thereon, by standard techniques known in the art. The contact angle of a hydrophobic metal oxide is preferably greater than 50°.

The metal oxide particles are preferably coated in order to render them hydrophobic. Suitable coating materials are water-repellent, preferably organic, and include fatty acids, preferably fatty acids containing 10 to 20 carbon atoms, such as lauric acid, stearic acid and isostearic acid, salts of the above fatty acids such as sodium salts and aluminium salts, fatty alcohols, such as stearyl alcohol, and silicones such as polydimethylsiloxane and substituted polydimethylsiloxanes, and reactive silicones such as methylhydrosiloxane and polymers and copolymers thereof. Stearic acid and/or salt thereof is particularly preferred. The organic coating may be applied using any conventional process. Typically, metal oxide particles are dispersed in water and heated to a temperature in the range 50°C to 80°C. A fatty acid, for example, is then deposited on the metal oxide particles by adding a salt of the fatty acid (e.g. sodium stearate) to the dispersion, followed by an acid. Alternatively, the metal oxide particles can be mixed with a solution of the water-repellent material in an organic solvent, followed by evaporation of the solvent. In an alternative embodiment of the invention, the water-repellent material can be added directly to the composition according to the present invention, during preparation thereof, such that the hydrophobic coating is formed in situ. Generally, the particles are treated with up to 25%, more preferably in the range from 3% to 20%, particularly 6% to 17%, and especially 10% to 15% by weight of organic material, preferably fatty acid, calculated with respect to the metal oxide core particles.

Alternatively or additionally, the particles of metal oxide may have an inorganic coating. For example, metal oxide particles, such as titanium dioxide, may be coated with oxides of other elements such as oxides of aluminium, zirconium or silicon, or mixtures thereof such as alumina and silica as disclosed in GB-2205088-A, the teaching of which is incorporated herein by reference. The preferred amount of inorganic coating is in the range from 2% to 25%, more preferably 4% to 20%, particularly 6% to 15%, and especially 8% to 12% by weight, calculated with respect to the weight of metal oxide core particles. The inorganic coating may be applied

UOI 51130

4

using techniques known in the art. A typical process comprises forming an aqueous dispersion of metal oxide particles in the presence of a soluble salt of the inorganic element whose oxide will form the coating. This dispersion is usually acidic or basic, depending upon the nature of the salt chosen, and precipitation of the inorganic oxide is achieved by adjusting the pH of the dispersion by the addition of acid or alkali, as appropriate.

In a preferred embodiment of the invention, the metal oxide particles are coated with both an inorganic and an organic coating, either sequentially or as a mixture. It is preferred that the inorganic coating, preferably alumina, is applied first followed by the organic coating, preferably fatty acid and/or salt thereof. Thus, preferred metal oxide particles for use in the present invention comprise (i) in the range from 60% to 98%, more preferably 65% to 95%, particularly 70% to 80%, and especially 72% to 78% by weight of metal oxide, preferably titanium dioxide, with respect to the total weight of the particles, (ii) in the range from 0.5% to 15%, more preferably 2% to 12%, particularly 5% to 10%, and especially 6% to 9% by weight of inorganic coating, preferably alumina, with respect to the total weight of the particles, and (iii) in the range from 1% to 21%, more preferably 4% to 18%, particularly 7% to 15%, and especially 9% to 12% by weight of organic coating, preferably fatty acid and/or salt thereof, with respect to the total weight of the particles. Such metal oxide particles provide a surprising combination of both improved photostability and dispersibility.

The individual or primary metal oxide particles are preferably acicular in shape and have a long axis (maximum dimension or length) and short axis (minimum dimension or width). The third axis of the particles (or depth) is preferably approximately the same dimensions as the width. The mean length by number of the primary metal oxide particles is suitably in the range from 50 to 90 nm, preferably 55 to 77 nm, more preferably 55 to 73 nm, particularly 60 to 70 nm, and especially 60 to 65 nm. The mean width by number of the particles is suitably in the range from 5 to 20 nm, preferably 8 to 19 nm, more preferably 10 to 18 nm, particularly 12 to 17 nm, and especially 14 to 16 nm. The primary titanium dioxide particles preferably have a mean aspect ratio $d_1:d_2$ (where d_1 and d_2 , respectively, are the length and width of the particle) in the range from 2.0 to 8.0:1, more preferably 3.0 to 6.5:1, particularly 4.0 to 6.0:1, and especially 4.5 to 5.5:1. The size of the primary particles can be suitably measured using electron microscopy. The size of a particle can be determined by measuring the length and width of a filler particle selected from a photographic image obtained by using a transmission electron microscope.

The metal oxide particles suitably have a mean crystal size (measured by X-ray diffraction as herein described) in the range from 4 to 10 nm, preferably 5 to 9 nm, more preferably 5.5 to 8.5 nm, particularly 6 to 8 nm, and especially 6.5 to 7.5 nm.

UQI 51130

5

The size distribution of the crystal size of the metal oxide particles can be important, and suitably at least 30%, preferably at least 40%, more preferably at least 50%, particularly at least 60%, and especially at least 70% by weight of the metal oxide particles have a crystal size within one or more of the above preferred ranges for the mean crystal size.

5

When formed into a dispersion according to the present invention, the particulate metal oxide suitably has a median volume particle diameter (equivalent spherical diameter corresponding to 50% of the volume of all the particles, read on the cumulative distribution curve relating volume % to the diameter of the particles - often referred to as the "D(v,0.5)" value)) (hereinafter referred to as dispersion particle size), measured as herein described, in the range from 24 to 42 nm, preferably 27 to 39 nm, more preferably 29 to 37 nm, particularly 31 to 35 nm, and especially 32 to 34 nm.

10

The size distribution of the metal oxide particles in dispersion can also be an important parameter in obtaining, for example, a sunscreen product having the required properties. In a preferred embodiment suitably less than 10% by volume of metal oxide particles have a volume diameter of less than 13 nm, preferably less than 11 nm, more preferably less than 10 nm, particularly less than 9 nm, and especially less than 8 nm below the median volume particle diameter. In addition, suitably less than 16% by volume of metal oxide particles have a volume diameter of less than 11 nm, preferably less than 9 nm, more preferably less than 8 nm, particularly less than 7 nm, and especially less than 6 nm below the median volume particle diameter. Further, suitably less than 30% by volume of metal oxide particles have a volume diameter of less than 7 nm, preferably less than 6 nm, more preferably less than 5 nm, particularly less than 4 nm, and especially less than 3 nm below the median volume particle diameter.

15

20

25

Also, suitably more than 90% by volume of metal oxide particles have a volume diameter of less than 30 nm, preferably less than 27 nm, more preferably less than 25 nm, particularly less than 23 nm, and especially less than 21 nm above the median volume particle diameter. In addition, suitably more than 84% by volume of metal oxide particles have a volume diameter of less than 19 nm, preferably less than 18 nm, more preferably less than 17 nm, particularly less than 16 nm, and especially less than 15 nm above the median volume particle diameter. Further, suitably more than 70% by volume of metal oxide particles have a volume diameter of less than 8 nm, preferably less than 7 nm, more preferably less than 6 nm, particularly less than 5 nm, and especially less than 4 nm above the median volume particle diameter.

30

35

Dispersion particle size of the metal oxide particles described herein may be measured by electron microscope, coulter counter, sedimentation analysis and static or dynamic light scattering. Techniques based on sedimentation analysis are preferred. The median particle

UQI 51130

6

size may be determined by plotting a cumulative distribution curve representing the percentage of particle volume below chosen particle sizes and measuring the 50th percentile. The median particle volume diameter and particle size distribution of the metal oxide particles in dispersion is suitably measured using a Brookhaven particle sizer, as described herein.

5

In a particularly preferred embodiment of the invention, the metal oxide particles have a BET specific surface area, measured as described herein, of greater than 40, more preferably in the range from 50 to 100, particularly 60 to 90, and especially 65 to 75 m²/g.

- 10 The metal oxide particles used in the present invention exhibit improved transparency suitably having an extinction coefficient at 524 nm (E_{524}), measured as herein described, in the range from 0.4 to 1.2, preferably 0.5 to 1.1, more preferably 0.6 to 1.0, particularly 0.7 to 0.9, and especially 0.75 to 0.85 l/g/cm. In addition, the metal oxide particles suitably have an extinction coefficient at 460 nm (E_{460}), measured as herein described, in the range from 0.8 to 2.2,
15 preferably 1.0 to 2.0, more preferably 1.2 to 1.8, particularly 1.3 to 1.7, and especially 1.4 to 1.6 l/g/cm.

- The metal oxide particles exhibit effective UV absorption, suitably having an extinction coefficient at 360 nm (E_{360}), measured as herein described, in the range from 5 to 11,
20 preferably 6 to 10, more preferably 6.5 to 9.5, particularly 7 to 9, and especially 7.5 to 8.5 l/g/cm. The metal oxide particles also suitably have an extinction coefficient at 308 nm (E_{308}), measured as herein described, in the range from 40 to 62, preferably 42 to 50, more preferably 43 to 49, particularly 44 to 48, and especially 45 to 46 l/g/cm.

- 25 The metal oxide particles suitably have a maximum extinction coefficient $E(\max)$, measured as herein described, in the range from 57 to 70, preferably 58 to 68, more preferably 59 to 66, particularly 60 to 64, and especially 61 to 62 l/g/cm. The metal oxide particles suitably have a $\lambda(\max)$, measured as herein described, in the range from 270 to 286, preferably 272 to 284, more preferably 274 to 282, particularly 276 to 280, and especially 277 to 278 nm.

30

- The metal oxide particles suitably exhibit reduced whiteness, preferably having a change in whiteness ΔL of a sunscreen product containing the particles, measured as herein described, of less than 3, more preferably in the range from 0.5 to 2.5, and particularly 1.0 to 2.0. In addition, a sunscreen product containing the particles preferably has a whiteness index,
35 measured as herein described, of less than 100%, more preferably in the range from 10% to 80%, particularly 20% to 60%, and especially 30% to 50%.

UQI 51130

7

The metal oxide particles suitably have reduced photogreying, preferably having a photogreying index, measured as herein described, of less than 15, more preferably in the range from 1 to 10, particularly 2 to 7, and especially 3 to 5.

5 In a dispersion according to the present invention, the metal oxide particles are stable to aggregation. The metal oxide particles in the dispersion are relatively uniformly dispersed and resistant to settling out on standing, but if some settling out does occur, the particles can be easily redispersed by simple agitation.

10 The dispersing medium used in the present invention preferably comprises a mixture of at least one polar organic material having an interfacial tension compared to water of less than 30 mNm^{-1} and at least one organic non-polar material having an interfacial tension of greater than 30 mNm^{-1} . The polar material suitably has an interfacial tension compared to water in the range from 5 to 27, preferably 15 to 25, more preferably 19 to 24, particularly 21 to 23, and
15 especially 21.5 to 22.5 mNm^{-1} . The non-polar material suitably has an interfacial tension in the range from 33 to 50, preferably 35 to 45, more preferably 36 to 43, particularly 37 to 40, and especially 38 to 39 mNm^{-1} .

The difference in the interfacial tension of the least one polar material and the least one non-polar material in a dispersion according to the present invention is suitably in the range from 5
20 to 35, preferably 10 to 25 more preferably 13 to 20, particularly 15 to 18, and especially 16 to 17 mNm^{-1} . The dispersing medium as a whole (i.e. mixture of polar and non-polar material) suitably has an interfacial tension in the range from 23 to 35, preferably 24 to 31, more preferably 25 to 29, particularly 25.5 to 28, and especially 26 to 27 mNm^{-1} .

25 The ratio of polar to non-polar dispersing medium present in the dispersion is suitably in the range from 10 to 90:10 to 90, preferably 20 to 80:20 to 80, more preferably 30 to 70:30 to 70, particularly 40 to 60:40 to 60, and especially 45 to 55:45 to 55% by weight.

30 Suitable polar materials comprise, or are selected from the group consisting of, C12-16 alkyl benzoate, caprylic/capric triglyceride, cetearyl isononanoate, ethylhexyl isostearate, ethylhexyl palmitate, isononyl isononanoate, isopropyl isostearate, isopropyl myristate, isostearyl isostearate, isostearyl neopentanoate, octyldodecanol, pentaerythrityl tetraistearate, PPG-15 stearyl ether, triethylhexyl triglyceride, dicaprylyl carbonate, ethylhexyl
35 stearate, helianthus annuus (sunflower) seed oil, isopropyl palmitate, and octyldodecyl neopentanoate. Preferred polar materials are triethylhexyl triglyceride, C12-16 alkyl benzoate, caprylic/capric triglyceride, isononyl isononanoate, isostearyl neopentanoate, and octyldodecyl neopentanoate, and particularly preferred is triethylhexyl triglyceride.

UQI 51130

8

Suitable non-polar materials comprise, or are selected from the group consisting of, C13-14 isoparaffin, isohexadecane, paraffinum liquidum (mineral oil), squalane, squalene, hydrogenated polyisobutene, and polydecene. Preferred non-polar materials are isohexadecane, hydrogenated polyisobutene, and squalane, and particularly preferred is isohexadecane.

The dispersion according to the present invention may also contain a dispersing agent in order to improve the properties thereof. The dispersing agent is suitably present in the range from 1% to 30%, preferably 2 to 20%, more preferably 3% to 10%, particularly 4 to 8%, and especially 5% to 7% by weight based on the total weight of metal oxide particles.

Suitable dispersing agents include substituted carboxylic acids, soap bases and polyhydroxy acids. Typically the dispersing agent can be one having a formula $X.CO.AR$ in which A is a divalent bridging group, R is a primary secondary or tertiary amino group or a salt thereof with an acid or a quaternary ammonium salt group and X is the residue of a polyester chain which together with the $-CO-$ group is derived from a hydroxy carboxylic acid of the formula $HO-R'-COOH$. As examples of typical dispersing agents are those based on ricinoleic acid, hydroxystearic acid, hydrogenated castor oil fatty acid which contains in addition to 12-hydroxystearic acid small amounts of stearic acid and palmitic acid. Dispersing agents based on one or more polyesters or salts of a hydroxycarboxylic acid and a carboxylic acid free of hydroxy groups can also be used. Compounds of various molecular weights can be used. Other suitable dispersing agents are those monoesters of fatty acid alkanolamides and carboxylic acids and their salts. Alkanolamides are based on ethanolamine, propanolamine or aminoethyl ethanolamine for example. Alternative dispersing agents are those based on polymers or copolymers of acrylic or methacrylic acids, e.g. block copolymers of such monomers. Other dispersing agents of similar general form are those having epoxy groups in the constituent radicals such as those based on the ethoxylated phosphate esters. The dispersing agent can be one of those commercially referred to as a hyper dispersant. Polyhydroxystearic acid is a particularly preferred dispersing agent.

An advantage of the present invention is that dispersions can be produced which contain at least 35, preferably at least 40, more preferably at least 45, particularly at least 50, especially at least 55, and generally up to 60% by weight of the total weight of the dispersion, of metal oxide particles.

The dispersions according to the present invention exhibit improved skin feel particularly when used to produce sunscreen products. Conventional sunscreen products exhibit a "greasy" afterfeel on the skin. Dispersions and sunscreen products according to the present invention

UQI 51130

9

surprisingly have improved skin feel, measured as herein described, for example conferring a significantly less greasy afterfeel.

5 A composition, preferably a sunscreen product, containing the dispersion of metal oxide particles defined herein suitably has a Sun Protection Factor (SPF), measured as herein described, of greater than 10, preferably greater than 15, more preferably greater than 20, particularly greater than 25, and especially greater than 30 and up to 40.

10 The dispersions of the present invention are useful as ingredients for preparing sunscreen compositions, especially in the form of emulsions. The compositions may further contain conventional additives suitable for use in the intended application, such as conventional cosmetic ingredients used in sunscreens. The particulate metal oxide as defined herein, may provide the only ultraviolet light attenuators in a sunscreen product according to the invention, but other suncreening agents, such as other metal oxides and/or other organic materials may
15 also be added. For example, the preferred titanium dioxide particles defined herein may be used in combination with other existing commercially available titanium dioxide and/or zinc oxide sunscreens. Suitable organic sunscreens for use with a composition according to the invention include p-methoxy cinnamic acid esters, salicylic acid esters, p-amino benzoic acid esters, non-sulphonated benzophenone derivatives, derivatives of dibenzoyl methane and
20 esters of 2-cyanoacrylic acid. Specific examples of useful organic sunscreens include benzophenone-1, benzophenone-2, benzophenone-3, benzophenone-6, benzophenone-8, benzophenone-12, Isopropyl dibenzoyl methane, butyl methoxy dibenzoyl methane, ethyl dihydroxypropyl PABA, glyceryl PABA, octyl dimethyl PABA, octyl methoxycinnamate, homosalate, octyl salicylate, octyl triazone, octocrylene, etocrylene, menthyl anthranilate, and
25 4-methylbenzylidene camphor.

In this specification the following test methods have been used:

1) Crystal Size Measurement of Metal Oxide Particles

30 Crystal size was measured by X-ray diffraction (XRD) line broadening. Diffraction patterns were measured with Cu K α radiation in a Siemens D5000 diffractometer equipped with a Sol-X energy dispersive detector acting as a monochromator. Programmable slits were used to measure diffraction from a 12 mm length of specimen with a step size of 0.02° and step counting time of 3 sec. The data was analysed by fitting the diffraction pattern between 22 and
35 48 °2 θ with a set of peaks corresponding to the reflection positions for rutile and, where anatase was present, an additional set of peaks corresponding to those reflections. The fitting process allowed for removal of the effects of instrument broadening on the diffraction line shapes. The value of the weight average mean crystal size was determined for the rutile 110 reflection (at approximately 27.4 °2 θ) based on its integral breadth according to the principles

UQI 51130

10

of the method of Stokes and Wilson (B. E. Warren, "X-Ray Diffraction", Addison-Wesley, Reading, Massachusetts, 1969, pp 254-257).

5 2) Median Particle Volume Diameter and Particle Size Distribution of Metal Oxide Particles in Dispersion

A dispersion of metal oxide particles was produced by mixing 6 g of polyhydroxystearic acid with 47 g of triethylhexyl triglyceride and 47 g of Isohexadecane, and then adding 100 g of metal oxide into the solution. The mixture was passed through a horizontal bead mill, operating at approximately 2100 r.p.m. and containing zirconia beads as grinding media for 15 minutes. The dispersion of metal oxide particles was diluted to between 30 and 40 g/l by mixing with isopropyl myristate. The diluted sample was analysed on the Brookhaven BI-XDC particle sizer in centrifugation mode, and the median particle volume diameter and particle size distribution measured.

15 3) BET Specific Surface Area of Metal Oxide Particles

The single point BET specific surface area was measured using a Micromeritics Flowsorb II 2300.

4) Change in Whiteness and Whiteness Index

20 A sunscreen formulation was coated on to the surface of a glossy black card and drawn down using a No 2 K bar to form a film of 12 μm wet thickness. The film was allowed to dry at room temperature for 10 minutes and the whiteness of the coating on the black surface (L_F) measured using a Minolta CR300 colourimeter. The change in whiteness ΔL was calculated by subtracting the whiteness of the substrate (L_S) from the whiteness of the coating (L_F). The whiteness index is the percentage change in whiteness ΔL compared to a standard titanium dioxide (= 100% value) (Tayca MT100T (ex Tayca Corporation)).

5) Photogreying Index

30 A metal oxide dispersion (15% by weight of metal oxide particles in C12-15 alkyl benzoate) was placed inside a 6 cm x 3 cm acrylic cell (containing a 2 cm x 1.5 cm space), and the cell made air tight by clamping a glass slide over the top, ensuring that no air bubbles were present. The initial whiteness (L_i) was measured using a Minolta CR300 colourimeter. The cell was then placed on a turntable revolving at 30 rpm and exposed to UV light for 2 hours (a UV lamp containing 4 TL29D,16/09 tubes mounted 12 cm from the cell), and the whiteness (L_T) remeasured. The photogreying index $\Delta L = L_i - L_T$.

6) Sun Protection Factor

The Sun Protection Factor (SPF) of a sunscreen formulation was determined using the *in vitro* method of Diffey and Robson, J. Soc. Cosmet. Chem. Vol. 40, pp 127-133, 1989.

UOI 51130

11

7) Extinction Coefficients

0.1 g sample of a metal oxide dispersion was diluted with 100 ml of cyclohexane. This diluted sample was then further diluted with cyclohexane in the ratio sample:cyclohexane of 1:19. The total dilution was 1:20,000. The diluted sample was then placed in a spectrophotometer (Perkin-Elmer Lambda 2 UV/VIS Spectrophotometer) with a 1 cm path length and the absorbance, of UV and visible light measured. Extinction coefficients were calculated from the equation $A=E.c.l$, where A =absorbance, E =extinction coefficient in litres per gram per cm, c =concentration in grams per litre, and l =path length in cm.

8) Interfacial Tension

Interfacial Tension between the polar or non-polar dispersing medium and water was measured by the Du Nuoy Ring method at 25°C.

9) Skin Feel

Skin feel was measured by trained assessors, using a protocol in which test samples were assigned % numerical scores for a series of sensory attributes. 2 ml of a metal oxide dispersion or sunscreen emulsion were spread over a circular area, approximately 5 cm in diameter, on the inner forearm. After spreading, the afterfeel (immediate and after 20 minutes) of the test sample on the skin was characterized in the following terms:- % "oily" skin feel; % "waxy" skin feel; % "greasy" skin feel; and % "silicone-like" skin feel.

The invention is illustrated by the following non-limiting examples.

Examples

Example 1

1 mole of titanium oxydichloride in acidic solution was reacted with 3 moles of NaOH in aqueous solution. After the initial reaction period, the temperature was increased to above 70°C, and stirring continued. The reaction mixture was neutralised by the addition of aqueous NaOH, and allowed to cool below 70°C. An alkaline solution of sodium aluminate was then added, equivalent to 10.5% by weight Al_2O_3 on TiO_2 weight. The temperature was maintained below 70°C during the addition. The temperature was increased to above 70°C, and sodium stearate equivalent to 13.5% by weight sodium stearate on weight of TiO_2 was added. The dispersion was neutralised by adding hydrochloric acid solution. The resultant slurry was filtered, washed with demineralised water, dried in an oven, and then micropulverised to produce particulate titanium dioxide.

A dispersion was produced by mixing 6 g of polyhydroxystearic acid with 47 g of triethylhexyl triglyceride and 47 g of isohexadecane, and then adding 100 g of titanium dioxide produced

UQI 51130

12

above into the solution. The mixture was passed through a horizontal bead mill, operating at approximately 2100 r.p.m. and containing zirconia beads as grinding media for 15 minutes.

The dispersion was subjected to the test procedures described herein, and the titanium dioxide exhibited the following properties:

i) Mean crystal size = 7 nm,

ii) 16% by volume of particles have a volume diameter of 8 nm below the median volume particle diameter,

30% by volume of particles have a volume diameter of 4.5 nm below the median volume particle diameter,

70% by volume of particles have a volume diameter of 6 nm above the median volume particle diameter,

84% by volume of particles have a volume diameter of 15 nm above the median volume particle diameter,

iii) Extinction Coefficients:

E_{624}	E_{450}	E_{308}	E_{280}	$E(\max)$	$\lambda(\max)$
0.8	1.5	45.1	7.1	61.4	277

Example 2

This titanium dioxide dispersion produced in Example 1 was used to prepare a sunscreen product having the following composition.

	<u>% w/w</u>
<u>Phase A:</u>	
ARLACEL P135 (ex Uniqema)	2.0
ESTOL 1512 (ex Uniqema)	16.7
30 Candelilla Wax (ex Eggar&Co Chemicals Ltd)	1.0
Titanium Dioxide dispersion produced above	15.0
<u>Phase B:</u>	
PRICERINE 9091 (ex Uniqema)	4.0
35 Magnesium Sulfate	0.7
Demineralised Water	60.1
<u>Phase C:</u>	
Germaben II	0.5

UQI 51130

13

The ingredients of oil phase A were mixed and heated to 75-80°C. The ingredients of aqueous phase B were mixed and heated to 75-80°C, and slowly added to phase A with intensive mixing, followed by stirring with a Silverson mixer for 2 minutes. The mixture was cooled to 45°C with intensive stirring, and the preservative phase C added. The mixture was further cooled to room temperature with stirring.

The sunscreen product was subjected to the test procedures described herein and exhibited the following properties:

- | | | |
|----|--------------------------|---|
| 10 | i) Greasy Skin Feel | 30% immediate (43% for conventional sunscreen)
38% after 20 minutes (47% for conventional sunscreen) |
| | ii) Whiteness ΔL | 1.1 |
| | Whiteness Index | 39% |
| 15 | iii) SPF | 25 |

The above examples illustrate the improved properties of a dispersion and sunscreen product according to the present invention.

20

25

30

35

UQI 51130

14

CLAIMS

1. A dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of
5 at least one polar material having an interfacial tension of less than 30 mNm^{-1} and at least one non-polar material having an interfacial tension of greater than 30 mNm^{-1} .
2. A dispersion according to claim 1 wherein the metal oxide particles have a mean crystal size in the range from 4 to 10 nm.
10
3. A dispersion according to either one of claims 1 and 2 wherein at least 40% by weight of metal oxide particles have a crystal size within the range 5 to 9 nm.
4. A dispersion according to any one of the preceding claims wherein less than 16% by
15 volume of metal oxide particles have a volume diameter of less than 9 nm below the median volume particle diameter.
5. A dispersion according to any one of the preceding claims wherein less than 30% by volume of metal oxide particles have a volume diameter of less than 5 nm below the median
20 volume particle diameter.
6. A dispersion according to any one of the preceding claims wherein more than 84% by volume of metal oxide particles have a volume diameter of less than 17 nm above the median volume particle diameter.
25
7. A dispersion according to any one of the preceding claims wherein more than 70% by volume of metal oxide particles have a volume diameter of less than 6 nm above the median volume particle diameter.
8. A dispersion according to any one of the preceding claims wherein the metal oxide
30 particles have an extinction coefficient at 524 nm in the range from 0.4 to 1.2 l/g/cm .
9. A dispersion according to any one of the preceding claims wherein the metal oxide particles have an extinction coefficient at 360 nm in the range from 5 to 11 l/g/cm .
35
10. A dispersion according to any one of the preceding claims wherein the metal oxide particles have an extinction coefficient at 308 nm in the range from 40 to 52 l/g/cm .

UQI 51130

15

11. A dispersion according to any one of the preceding claims wherein the metal oxide particles have (i) a median volume particle diameter in the range from 29 to 37 nm, and/or (ii) less than 10% by volume of particles having a volume diameter of less than 11 nm below the median volume particle diameter, and/or (iii) less than 16% by volume of particles having a volume diameter of 8 nm below the median volume particle diameter, and/or (iv) less than 30% by volume of particles having a volume diameter of less than 5 nm below the median volume particle diameter, and/or (v) more than 90% by volume of particles having a volume diameter of less than 27 nm above the median volume particle diameter, and/or (vi) more than 84% by volume of particles having a volume diameter of less than 17 nm above the median volume particle diameter, and/or (vii) more than 70% by volume of particles having a volume diameter of less than 6 nm above the median volume particle diameter.
12. A dispersion according to any one of the preceding claims wherein the particles of metal oxide have an extinction coefficient at 524 nm in the range from 0.5 to 1.1 l/g/cm, an extinction coefficient at 450 nm in the range from 1.0 to 2.0 l/g/cm, an extinction coefficient at 360 nm in the range from 6 to 10 l/g/cm, an extinction coefficient at 308 nm in the range from 44 to 48 l/g/cm, a maximum extinction coefficient in the range from 60 to 64 l/g/cm, and a $\lambda(\text{max})$ in the range from 274 to 282 nm.
13. A dispersion according to any one of the preceding claims wherein the polar material has an interfacial tension in the range from 10 to 25 mNm⁻¹.
14. A dispersion according to any one of the preceding claims wherein the non-polar material has an interfacial tension in the range from 35 to 45 mNm⁻¹.
15. A dispersion according to any one of the preceding claims wherein the difference in the interfacial tension of the polar material and the non-polar material is in the range from 13 to 20 mNm⁻¹.
16. A dispersion according to any one of the preceding claims wherein the ratio of polar to non-polar material is in the range from 30 to 70:30 to 70% by weight.
17. A dispersion according to any one of the preceding claims wherein the polar material is selected from the group consisting of are triethylhexyl triglyceride, C12-15 alkyl benzoate, caprylic/capric triglyceride, isononyl isononanoate, isostearyl neopentanoate, and octyldodecyl neopentanoate.

UQI 51130

16

18. A dispersion according to any one of the preceding claims wherein the non-polar material is selected from the group consisting of isohexadecane, hydrogenated polyisobutene, and squalane.

5 19. A dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of (i) at least one polar material selected from the group consisting of, C12-15 alkyl benzoate, caprylic/capric triglyceride, cetearyl isononanoate, ethylhexyl isostearate, ethylhexyl palmitate, isononyl isononanoate, isopropyl isostearate, isopropyl myristate, isostearyl isostearate, 10 isostearyl neopentanoate, octyldodecanol, pentaerythrityl tetraisoate, PPG-15 stearyl ether, triethylhexyl triglyceride, dicaprylyl carbonate, ethylhexyl stearate, helianthus annus (sunflower) seed oil, isopropyl palmitate, and octyldodecyl neopentanoate, and (ii) at least one non-polar material selected from the group consisting of, C13-14 isoparaffin, isohexadecane, paraffinum liquidum (mineral oil), squalane, squalene, hydrogenated polyisobutene, and 15 polydecene.

20. A sunscreen product formed from a dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of at least one polar material having an interfacial tension 20 of less than 30 mNm^{-1} and at least one non-polar material having an interfacial tension of greater than 30 mNm^{-1} .

21. A sunscreen product comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, and (i) at least one polar material selected 25 from the group consisting of are triethylhexyl triglyceride, C12-15 alkyl benzoate, caprylic/capric triglyceride, isononyl isononanoate, isostearyl neopentanoate, and octyldodecyl neopentanoate, and (ii) at least one non-polar material selected from the group consisting of isohexadecane, hydrogenated polyisobutene, and squalane.

30 22. The use of a dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of at least one polar material having an interfacial tension of less than 30 mNm^{-1} and at least one non-polar material having an interfacial tension of greater than 30 mNm^{-1} , to produce a sunscreen having improved skin feel.

35

23. The use of a dispersion comprising particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm, dispersed in a medium which comprises a mixture of at least one polar material having an interfacial tension of less than 30 mNm^{-1} and at

UQI 51130

17

least one non-polar material having an interfacial tension of greater than 30 mNm^{-1} , in the manufacture of a transparent sunscreen having improved skin feel.

5

10

15

20

25

30

35

UQI 51130

18

ABSTRACT

5 A dispersion contains particles of metal oxide having a median volume particle diameter in the range from 24 to 42 nm which are dispersed in a medium which includes a mixture of at least one polar material having an interfacial tension of less than 30 mNm^{-1} and at least one non-polar material having an interfacial tension of greater than 30 mNm^{-1} . The dispersion can be used in a sunscreen product that exhibits effective UV protection, transparency, and improved skin feel.

10